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Agriculture, Ecosystems and Environment 99 (2003) 187–199
Agriculture Ecosystems & Environment
www.elsevier.com/locate/agee

Modification of phosphorus export from an eastern USA catchment by fluvial sediment and phosphorus inputs

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Received 27 August 2002; received in revised form 22 January 2003; accepted 19 February 2003

Abstract

Phosphorus (P) export from agricultural catchments can accelerate freshwater eutrophication. Landscape-based remedial measures can reduce edge-of-field P losses. However, stream channel hydraulics and fluvial sediment properties can modify the forms and amounts of P exported by the time it reaches the catchment outlet. This study examines if land use, fluvial sediment properties, and storm flow dissolved and particulate P are interdependent within a mixed land use catchment in Pennsylvania, USA, so that remedial strategies can be most effectively targeted within the catchment to mitigate P export. Samples of the top 2–3 cm of stream-bed sediments ($n = 40$) were collected in April 2001, above and below tributary confluences and in areas of likely deposition. Stream water samples were collected at each of 23 sub-watershed outlets during base ($n = 7$) and storm flow ($n = 3$) events between 2000 and 2002. The P content and sorptive properties of deposited fluvial sediments varied among tributaries and flow regimes. Total P of sediments in tributaries (322 mg kg^{-1}) was greater than below confluences (239 mg kg^{-1}), whereas dissolved P release rate was lower (92 and 166 mg P kg^{-1} min^{-1}, respectively). This was attributed to physical disturbance by turbulent mixing and presence of more sand-sized particles at confluences (747 g kg^{-1}) than tributaries (707 g kg^{-1}). The percent cropped ($r = 0.51$) and forest ($r = -0.57$) land was related to the Mehlich-3 extractable P concentration of outflow sediment for each sub-catchment. This in turn influenced sediment P release, which was related to base flow P when sediments establish a quasi-equilibrium with flowing water within the catchment. However, storm flow P was not related to any sediment P properties but to percent of each sub-catchment in cropland ($r = 0.58$), reflecting the importance of erosion in P transport. Storm flow suspended sediment was related to sub-catchment area in crop ($r = 0.78$). To gain a better understanding of processes controlling P transport within and from a catchment and, thus, mitigation of losses, measures such as conservation tillage, manure management, and buffer strips, fluvial sediment properties as well as landscape management must be considered.
Published by Elsevier B.V.

Keywords: Eutrophication; Non-point sources; Overland flow; P desorption; P sorption; Remedial measures; Stream-bed sediments; Stream flow; Water quality

1. Introduction

Phosphorus (P), an essential nutrient for crop and animal production, can accelerate freshwater eutrophication (Carpenter et al., 1998; Sharpley, 2000a). Recently, the USEPA (1996) identified accelerated

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0167-8809/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/S0167-8809(03)00142-7

eutrophication as the most ubiquitous water quality impairment in the US, with agriculture a major contributor of P (USGS, 1999). Eutrophication restricts water use for fisheries, recreation, industry, and municipalities due to the increased growth of undesirable algae and aquatic weeds and oxygen depletion caused by their death and decomposition. Given general environmental concerns from harmful algal blooms (Burkholder and Glasgow, 1997) and regulatory pressure to reduce P loadings to surface waters via implementation of total maximum daily loads (TMDLs) (USEPA, 2000), a better understanding of factors controlling P loss from agricultural land and role of deposited fluvial sediments on the forms and amounts of P exported from a catchment is needed.

The bioavailability of fluvial sediment P to aquatic flora and fauna is central to the onset of accelerated eutrophication. However, the bioavailability of sediment bound P is indicative of a series of complex chemical and physical processes that can reflect sediment origin and history of land use. For instance, mechanisms that control suspended sediment transport in terrestrial overland flow and in fluvial systems tend to favor the relocation of finer-sized or low-density particles or flocs (Droppo et al., 2000; Beuselinck et al., 2000; Walling et al., 2000). Quite often these sediments are highly sorptive and carry with them much P (McDowell and Sharpley, 2002a). However, the enhanced sorption strength of fines compared to coarser materials implies that sorbed P is also much less likely to desorb into solution.

Coupled with these chemical processes, the transport of fluvial sediment is strongly influenced by the velocity and shear of flow, and aggregate stability of the sediment. Consequently, the contribution of two tributaries to P loss can differ not only by the source of transported sediment, but also according to the relative velocity of flow, causing turbidity at the confluence of two water bodies.

The interaction between these different processes can be complex. For instance, a large quantity of P can come from agricultural runoff compared to non-agricultural runoff, such as native forest. The sediments in agricultural runoff are likely to contain different organic matter concentrations and compositions, which affect particle size structure and aggregation and be much more enriched with P compared to sediments derived from forested land, low in P and a potential P sink. Therefore, land use can compete with fluvial transport processes as a major determinant of P bioavailability and/or nutrient enrichment of downstream water bodies.

The analysis of fluvial sediment enables the likely end-impact of P inputs and sources at various scales to be examined. This will help to identify and target P sources for remediation without the expense, labor and short-term variation inherent in taking a “blanket” catchment approach to mitigating P loss by examining every input and source of P within a catchment. For example, widespread implementation of remedial measures such as stream buffers, manure storage, conservation tillage, and eroding gully treatment directed mainly at decreasing sediment and associated P loss, had little impact on lowering P export from catchments within the Chesapeake Bay Basin (Boesch et al., 2001) and Little Washita River Basin, Oklahoma (Sharpley and Smith, 1994).

This paper describes a study to determine if land use and/or chemical and physical properties of source sediments were related to the behavior of P in fluvial sediments and stream waters for a mixed land use catchment in central Pennsylvania, USA. A secondary objective was to identify where it would be most effective to implement remedial strategies within the catchment to mitigate P loss and estimate the potential for the fluvial system to buffer changes in P load.

2. Materials and methods

2.1. Catchment characteristics

Catchment WE-38 is characteristic of mixed agricultural and forested uplands common within the Appalachian Province and Piedmont Plateau of the eastern USA (Fig. 1). The catchment (7.4 km^2) has contained within it 23 sub-catchments ranging in area from 0.042 to 1.1 km^2, and has been studied since 1968 in numerous publications. These publications describe in detail, catchment hydrology, topography, geology and land use (e.g. Pionke and Urban, 1985; Gburek, 1990; Pionke et al., 2000). Briefly, WE-38 is located 40 km north of Harrisburg, Pennsylvania, USA, within the Susquehanna River Basin, which supplies nearly half of the flow to the Chesapeake Bay. Elevations range from about 240 m (m.s.l.) in the south to about

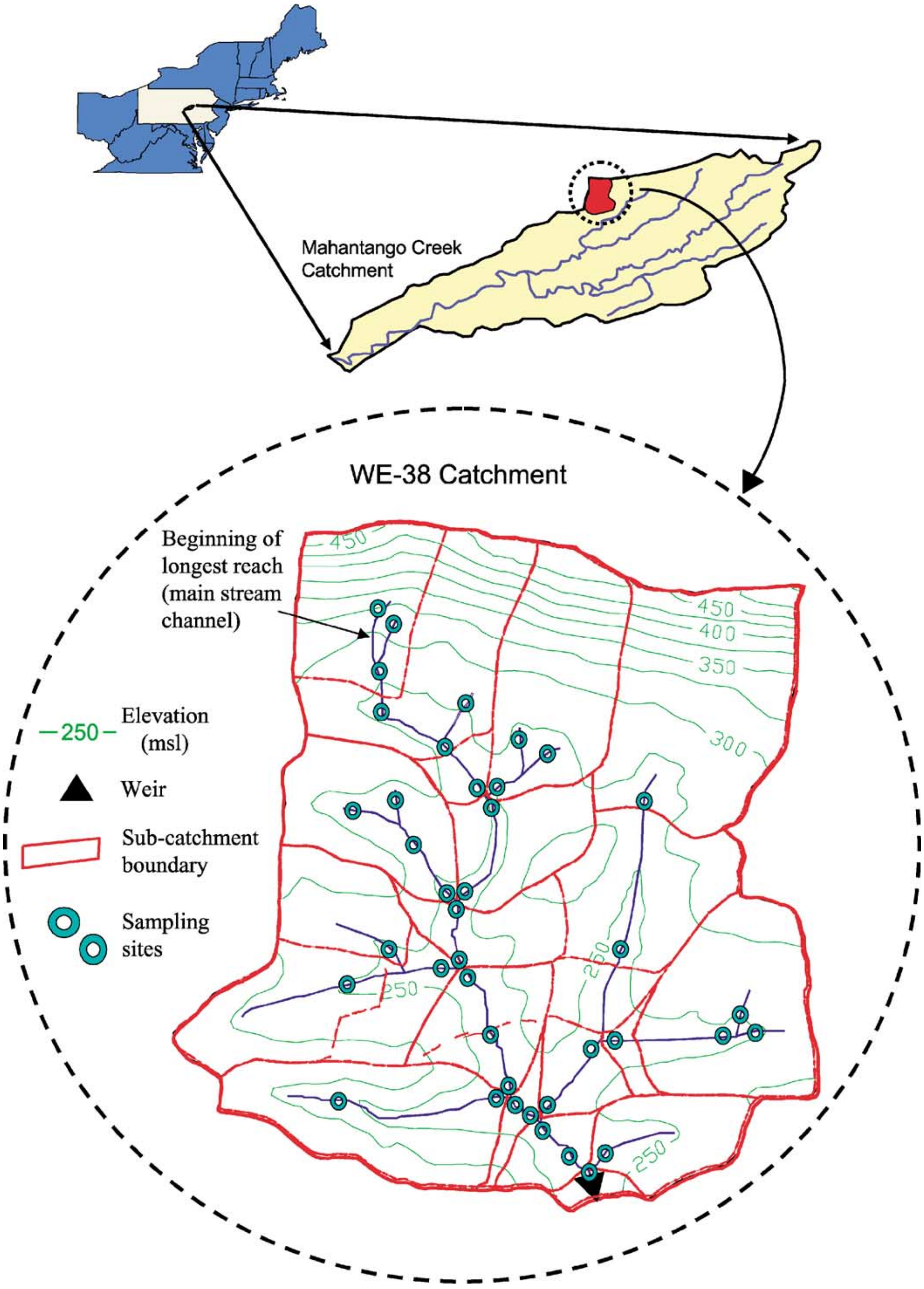

Fig. 1. Sediment sampling sites and sub-catchment boundaries within catchment WE-38. *Note*: Sub-catchment water samples were taken at their respective outflows.

480 m (m.s.l.) in the north, while slopes range from 3 to 17%. Land use is dominated by agriculture among 285 delineated fields, with 60% of the catchment in cropland and 10% in pasture. The remaining 30% of the catchment is deciduous forest. Conventionally tilled crops grown in the catchment include 25% corn (*Zea mays* L.), 15% soybean (*Glycine max* (L.) Merr.), 13% wheat (*Triticum aestivum* L.), oats (*Avena* L. Poaceae), and barley (*Hordeum* L. (Poaceae)), and 7% alfalfa (*Medicago* L. (Fabaceae)). The majority of livestock production is conducted in a dairy and a swine operation. Nitrogen and P in manure (largely swine) and fertiliser are regularly applied in various quantities to cropland. Surveys of land use, livestock numbers and nutrient additions are made annually.

Soils within the catchment range in depth from 75 to 150 cm. Soils are mostly silt loam Luvisols and deepest in areas likely to produce overland flow either by saturation- or infiltration-excess mechanisms (Srinivasan et al., 2002). These areas are near streams and often contain fragipans and high water tables (Pionke et al., 2000). Precipitation is about 1100 mm year and stream flow about 450 mm per year. Approximately, 10–20% of stream flow from the catchment is from overland flow (controlled by variable source area hydrology: Ward, 1984), the remainder subsurface flow. Residence time of subsurface flow through the catchment is short (1–3 years) due to high transmissivities and small water storage capacity dictated by fracture, rather than matrix, porosity (Pionke et al., 2000).

2.2. Fluvial sediment and water collection

Sediments were sampled in triplicate in April 2001, using an Eckman dredge from the top 2–3 cm of the stream-bed at 40 sites before and after confluences and in areas of likely deposition within a tributary (Fig. 1). Triplicate sediment samples were combined, passed through a 4 mm screen to remove large materials, and stored wet at 5 °C until analysis (within 7 days). During 2000–2002, a total of 10 stream water samples were collected (about 250 ml) from the outlet of each sub-catchment, filtered (<0.45 μm) and stored at 5 °C in the dark until analysis (within 3 days). Seven of the events were taken during base flow, at 4-month intervals, while the remaining events were during distinct storm flow events and sampled during the rising limb of the hydrograph monitored at the catchment WE-38 outflow. Flow rates at each sampling site were assumed to reflect flow at the outlet of WE-38.

2.3. Sediment and stream water analyses

A sub-sample of each wet sediment was oven dried (105 °C) to determine moisture content. Mehlich-3 soluble Al, Fe, Ca and P concentration of sediments was determined by end-over-end shaking whole wet sediments (equivalent of 1 g dry weight) with 10 ml of 0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3, and 0.001 M EDTA for 5 min (Mehlich, 1984), filtering (Whatman no. 42 filter paper), and analysing the extract via inductively coupled plasma-mass adsorption spectrometry. Phosphorus speciation was determined using a modified Hieltjes and Lijklema (1980) sequential extraction regime. To 500 mg of sediment (dry weight equivalent), 15 ml of 1 M NH_4Cl was added and the suspension shaken overnight (20 h). After shaking, the suspension was centrifuged 2500 × *g* for 10 min and the supernatant decanted off. This process was repeated with additional 0.1 M NaOH (twice) and then with 1.0 M HCl. These fractions represent readily labile P (NH_4Cl-P), P bound by Al and Fe oxides and humic materials (NaOH-P) and calcium bound P (HCl-P). A sub-sample of the NaOH extract was digested (Taylor, 2000) to give total P extracted and organic P (NaOH-P_{org}) by difference from inorganic P (NaOH-P). Samples of oven-dried (378 K) soil were also analyzed for total P after Kjeldhal digestion (Taylor, 2000). Phosphorus in all neutralized extracts was determined by the method of Watanabe and Olsen (1965).

Whole wet sediments (1 g dry weight equivalent) were mixed with 20 ml of 0.003 M $CaCl_2$ solutions (equivalent to ionic strength of stream water, Klotz, 1988) containing graduated concentrations (0, 1, 2, 4, 10, 20, and 50 mg P ml^{-1}) of P (as KH_2PO_4) and shaken for 16 h. Samples were then filtered (<0.45 μm) and P determined using the method of Murphy and Riley (1962). The Langmuir equation was used to obtain estimates of the P sorption maximum (P_{max}, mg kg^{-1}) and the P affinity parameter (binding strength, *k*, mg P l^{-1}). The initial slope of a graph of P sorption (mg kg^{-1}) against P in solution (mg l^{-1}) was used to estimate equilibrium P concentration (mg l^{-1}, EPC_0) as the solution P concentration at which no net sorption or desorption ($0\,mg\,kg^{-1}$) occurred.

The kinetics of P release were studied by shaking soil (1 g dry weight equivalent) in 0.003 M $CaCl_2$ (equivalent to ionic strength of stream water, Klotz, 1988) for periods of 10 min, 30 min, 4 h, and 16 h before filtering (<0.45 μm) and measuring P desorbed. Desorption data was fitted to an Elovich equation:

$$Q = \frac{[\ln(\alpha\beta) + \ln(t)]}{\beta} \quad (1)$$

where Q is the amount of P desorbed ($mg\,kg^{-1}$) at time t (min) and α and β are constants. The constant β can be used as an index of release rate ($mg\,kg^{-1}$ soil min^{-1}), such that as the value of β increases the rate of P release increases (Steffens, 1994).

Filtered stream water samples were analyzed for dissolved reactive P (DRP) and total dissolved reactive P (TDP) after a Kjeldhal digestion (Taylor, 2000). An unfiltered sample was also digested and total P (TP) measured within 7 days. Dissolved unreactive P (DURP) was defined as the difference between TDP and DRP and particulate P (PP) as TP less TDP, respectively. An additional measurement was made of suspended sediment.

Statistical analyses (one-way analysis of variance, correlation coefficients, curve fits, means and standard errors) were performed with SPSS version 10.0 (SPSS Inc., 1999). All r^2 values of the fit of the Elovich equation to kinetics data were significant ($P < 0.05$) and greater than 0.948.

3. Results and discussion

3.1. Comparison among flow regimes and physiochemical parameters

Physiochemical characteristics and comparative analysis of sediments within the longest reach of the main stream channel within the catchment (Fig. 1), sediments in tributaries, and sediments just after the confluence of a tributary are given in Table 1. Significant differences ($P < 0.05$) were noted for a number of parameters between sediment classes, as defined by location and flow regime. A major difference of note between tributaries and the main stream is the greater total P and Mehlich-3 extractable P concentrations of the tributary sediments (Table 1). However, the EPC_0 of main fluvial sediments is on average,

Table 1
Mean (±S.E.) physiochemical parameters for different flow regimes (the longest single reach; $n = 16$, tributaries; $n = 27$, confluence; $n = 8$, and all samples combined (overall); $n = 40$) for the stream sediments sampled within WE-38 (see Fig. 1 for locations)

Parameter	Single reach	Tributaries	Confluence	Overall
pH	6.9 (0.1) a	6.8 (0.1) a	6.8 (0.1) a	6.8 (0.1) a
Sand ($g\,kg^{-1}$)	769 (17) a	707 (21) b	747 (20) a	719 (17) b
Silt ($g\,kg^{-1}$)	84 (12) a	120 (15) b	101 (16) b	114 (12) b
Clay ($g\,kg^{-1}$)	147 (8) a	173 (8) b	153 (9) a	167 (6) b
Fines (silt + clay) ($g\,kg^{-1}$)	231 (2) a	293 (21) b	252 (19) a	281 (17) a
Organic matter ($g\,kg^{-1}$)	24 (2) a	41 (4) b	27 (3) a	37 (3) a
Mehlich-3 Al ($mg\,kg^{-1}$)	323 (21) a	478 (37) b	403 (35) b	457 (30) b
Mehlich-3 Fe ($mg\,kg^{-1}$)	334 (48) a	374 (37) a	302 (56) a	354 (31) a
Mehlich-3 Ca ($mg\,kg^{-1}$)	416 (37) a	664 (67) b	471 (46) a	615 (54) b
Mehlich-3 P ($mg\,kg^{-1}$)	31 (5) a	41 (4) b	34 (8) b	38 (4) b
β ($mg\,kg^{-1}\,min^{-1}$)	136 (22) a	92 (9) b	166 (36) a	110 (12) ab
Total desorption potential	2373 (174) a	1954 (160) b	2634 (254) a	2114 (140) b
EPC_0 ($mg\,l^{-1}$)	0.050 (0.003) a	0.048 (0.004) a	0.050 (0.003) a	0.047 (0.003) a
P_{max} ($mg\,kg^{-1}$)	169 (11) a	216 (15) b	183 (11) a	208 (12) ab
NaOH-P ($mg\,kg^{-1}$)	102 (10) a	139 (11) b	112 (14) a	132 (9) b
NaOH-P_{org} ($mg\,kg^{-1}$)	43 (4) a	69 (8) b	43 (6) a	63 (6) b
HCl-P ($mg\,kg^{-1}$)	29 (4) a	38 (5) a	29 (5) a	36 (4) a
Residual-P ($mg\,kg^{-1}$)	51 (7) a	76 (7) b	55 (9) a	71 (1) b
Total-P ($mg\,kg^{-1}$)	224 (19) a	322 (26) b	239 (22) a	302 (21) b

Different letters within a row indicate significant difference between flow regimes at $P < 0.05$ level (one-way analysis of variance).

slightly higher than of tributary sediments. This can be explained by the greater proportion of sand in the main fluvial sediments compared to the tributary sediments. It is well known that fine-sized (<63 μm) particles sorb more P and release P less readily than coarser-sized fractions (Stone and Murdoch, 1989; McDowell and Sharpley, 2002a).

In streams with good hydraulic mixing, a state of quasi-equilibrium exists under conditions of low or base flow, whereby the kinetics of P release or uptake are nearly complete by the time a volume of water flows by. During base flow, EPC_0 will influence stream P concentration, whereby P will desorb from sediments if P concentration in flow is less than the sediment's EPC_0. Conversely, P in stream flow will be sorbed by sediments if stream P concentration is greater than sediment EPC_0 (Kunishi et al., 1972). In the present study, mean DRP in base flow was related to EPC_0 ($r^2 = 0.50$; $P < 0.001$) (Fig. 2). Conversely, storm flow DRP concentration was not related to sediment EPC_0, due to the greater influence of P inputs associated with suspended sediments and an inability of the sediments to reach a kinetic quasi-equilibrium with stream flow.

Variability in sediment EPC_0 along a stream or river channel is characteristically high, reflecting physical hydraulic processes, management of land adjacent to the stream and form of P occurring in the sediment. Indeed, land use was significantly correlated to a measure of plant available P (Mehlich-3 extractable P) in sediments at the outflow of each sub-catchment. For instance, the proportion of land in crop was positively correlated to the Mehlich-3 P concentration of outflow sediment ($r = 0.51^*$), while the proportion of land in forest was negatively correlated ($r = -0.57^{**}$). It is well known that forest land compared to cropland has a mitigating effect on P and sediment movement (e.g. Peterjohn and Correll, 1984).

At the confluence of two streams, and for a certain distance downstream, one would expect the greater turbulence and shearing forces to cause a shift in P associated with sediment and available to flow towards coarser-sized fractions, whereas mobile fine-sized fractions are washed away. The data shows some evidence to support this. Total P and the percent sand in sediment from or near a confluence were less and greater than that measured in the tributary sediments, respectively. However, the data suggests that the

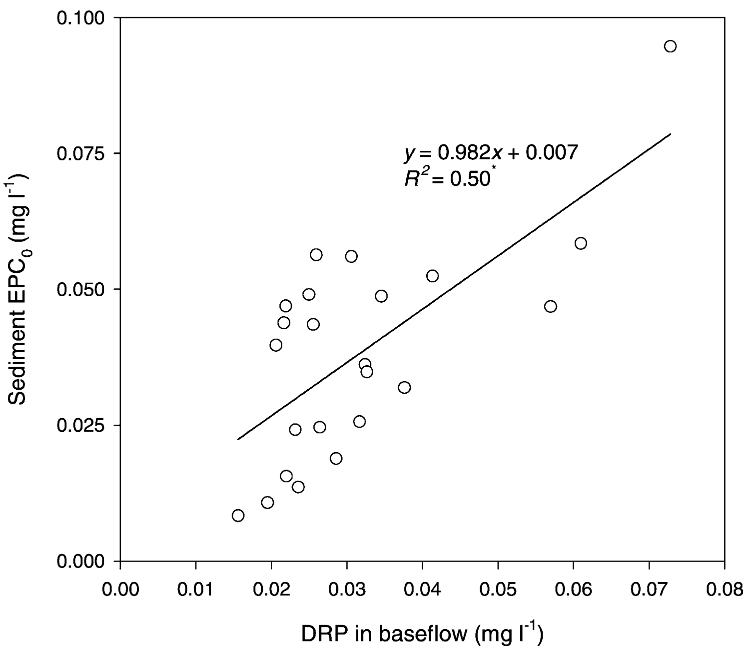

Fig. 2. The relationship between DRP in base flow and sediment EPC_0.

degree of mixing is not great, as the percentage sand is less than and total P greater than that measured in the main stream sediments. While it should be mentioned that the influence of physical processes varies greatly from site to site, we can say that on average, P availability from the tributaries is diluted by and thus, mediated by main stream sediments.

3.2. The influence of sediment P chemistry on stream P concentrations

Correlation coefficients between sediment uptake (sorption) and release (desorption) parameters and likely physiochemical parameters are given in Table 2. Contrary to previous findings (e.g. McDowell and Sharpley, 2001a), no significant correlation was found between chemical constituents such as Mehlich-3 extractable Fe and EPC_0. The role of Fe has long been considered a major controlling factor in sediment P uptake (e.g. Eckerrot and Pettersson, 1993). Indeed, sequential extraction data indicates that a large proportion sediment P is NaOH extractable, which represents P bound to Al and Fe oxides and humic substances (Zhang and Kovar, 2000). Nevertheless, NaOH-P and Mehlich-3 extractable Fe clearly represent fractions that are not sensitive to the expression of EPC_0 in these sediments. However, a good correlation was found between EPC_0 and sediment physical characteristics, specifically the proportion of sand in the sediment. As mentioned earlier, sand greatly affects the release of P, which is much quicker than from finer-sized particles. Similar to P, the majority of Fe and Al is contained within these fine-sized particles. Thus, it is possible that chemical tests of the whole sediment are not selective enough of those particle sizes dominating sediment P characteristics (Sharpley, 2000b).

Consideration of particle size and the physical distribution of sand in sediments along the stream-bed must be taken into consideration when determining the expression of EPC_0. Sediment can be a significant source of P to stream flow if sediment EPC_0 is greater than stream flow P concentration, even when inputs from runoff have ceased. The long-term reservoir of P able to contribute to EPC_0 can be approximated from measures of sorbed P in the sediment or sorption maximum (P_{max}). Although, correlated to sediment particle-size distributions, P_{max} was more strongly correlated (greater level of significance) with sediment chemical properties, such as Mehlich-3 extractable Al and Ca, but especially organic matter content. This is probably a reflection of P sorbed by Al associated with organic matter (Parfitt, 1978). Indeed, a good correlation was evident between P_{max} and $NaOH_{org}$ ($r = 0.74^{***}$). While $NaOH_{org}$ represents on average, a third of P extracted by NaOH (Table 1), it would

Table 2
Correlation coefficients between P sorption and release characteristics, and possible controlling parameters for all sediments

Parameter	Bed sediment		
	EPC_0 (mg l^{-1})	P_{max} (mg kg^{-1})	β, release rate (mg kg^{-1} min^{-1})
pH	–[a]	0.34*	–
Sand (g kg^{-1})	0.71***	0.43**	0.46**
Silt (g kg^{-1})	0.50**	0.44**	0.37*
Clay (g kg^{-1})	0.49**	–	0.46**
Fines (silt + clay) (g kg^{-1})	0.56***	0.55***	0.48**
Organic matter	–	0.90***	0.38*
Mehlich-3 P (mg kg^{-1})	–	–	0.71***
Mehlich-3 Al (mg kg^{-1})	–	0.87***	–
Mehlich-3 Fe (mg kg^{-1})	–	0.32*	0.55***
Mehlich-3 Ca (mg kg^{-1})	–	0.72***	0.54***
P saturation (%)[b]	–	0.37*	0.55***

[a] The symbol '–' means not significant.
[b] P saturation given as the percentage ratio of $P/[1/3 \times (Al + Fe + Ca)]$ in mmol kg^{-1}.
* $P < 0.05$.
** $P < 0.01$.
*** $P < 0.001$.

appear that humic substances play an important role in determining the P_{max} of these sediments.

In addition to organic matter, a significant correlation and a good proportion of variation in P_{max} was explained by Mehlich-3 extractable Ca. This is also reflected by the near-neutral pH of the sediments. The presence and control of P by Ca and Al precipitates was explained by House and Denison (2000) arising from the formation of compounds such as octacalcium phosphate and vivianite. Numerous other studies have identified Ca-P precipitates and ionic strength effects as important regulators of P in streams (e.g. Klotz, 1991; McDiffett et al., 1989, Froelich, 1988). However, Klotz (1991) also noted that the effect of Ca on stream P concentrations was greater expressed in sediments with lesser organic matter and in-turn, biological activity. Other workers have also highlighted the role of microbial biomass in controlling P dynamics (e.g. Gächter and Meyer, 1993; Baldwin et al., 1997; Khoshmanesh et al., 1999). The significant correlation between organic matter and the uptake of P in our sediment would also suggest biotic processes were involved. Preliminary work has indicated that up to 35% of the P sorbed during flow may be housed by microbes in these sediments (McDowell and Sharpley, 2003). A value similar to that found by Khoshmanesh et al. (1999); however, additional work is needed to fully quantify the role of biotic processes in P uptake over the wide range of conditions and sediments as sampled here.

In the short to medium-term, P release from sediment to solution is a function of the kinetics of P desorption and size of the bioavailable P pool. For soils, the total quantity of P desorbable by repeated extractions with Fe-oxide strips that estimate of bioavailable P (Sharpley, 1993), can be estimated with Mehlich-3 extractable P (McDowell and Sharpley, 2002b). Therefore, combining P release rate (β, $\mathrm{mg\,kg^{-1}\,min^{-1}}$) with Mehlich-3 extractable P, should give a measure of overall (total) P desorption and potential for sediment to supply overlying water with P (provided stream flow P concentration drops below the EPC_0 of the sediment). The data in Table 1 shows that on average, main stream sediments had a greater total P desorption potential than sediment from the tributaries, despite a lesser mean total P concentration. Mehlich-3 extractable P of the tributary sediments is also greater than the average concentration in main stream sediments and emphasizes the influence of physical availability to flow, a reflection of the quicker release rate and greater proportion of sand in main stream sediments. Our data also shows that release rate, much the same as in soils, increases as a function of the bioavailable P pool, in this case Mehlich-3 extractable P concentration (Table 2; McDowell and Sharpley, 2002b).

3.3. The role of the landscape and in-stream processes in stream P concentrations

Over the last 10–15 years there has been increasing emphasis placed on combining landscape variables with management practices in tools and models aimed at better locating and then mitigating areas within a catchment most likely to contribute to P loss (e.g. Gburek et al., 2000; Sharpley et al., 2002). One such tool, the P index, is being widely used in the USA as a compromise between sound scientific theory on P loss, and current management by the land user (McDowell et al., 2001; Sharpley et al., 2001). This is a flexible approach that leaves scope for the user to locate where remedial strategies should be placed to be most effective and thus, learn their likely effect on P losses.

However, management of sources of nutrient export from landscapes at risk in catchments, also has limitations. One major omission in considering and managing edge-of-field losses is that the influence of uptake or release of P by fluvial sediments on P export is not accounted for (McDowell et al., 2001; Sharpley et al., 2002). This has the potential to be a considerable source of error when looking at catchments of different scale. For instance, in a review of land use and sediment yield, Walling (1999) indicated that fluvial systems have considerable capacity to buffer changes in sediment delivery, whereby rivers with a low sediment delivery ratio will exhibit a large buffering capacity and vise versa. As P is readily sorbed and largely associated with sediment the potential for confusion is clear, especially in catchments with much natural sediment movement.

At the core of many tools and models used to predict P loss is the premise that an increase in agricultural intensification, especially as cropland, leads to an increase in P loss (Carpenter et al., 1998). Conversely, a greater proportion of land within a catchment in forestry should lose less P. For example, in a study of 12 catchments within an area of

Table 3
Summary statistics for sub-catchments within the main WE-38 catchment

Parameter	Minimum	Maximum	Mean	S.E.M.[a]
All sub-catchments				
Total area (km^2)	0.04	1.1	2.3	0.42
Forest (%)	4	95	54	5.2
Cropland/pasture (%)[b]	5	96	43	4.6
Slope (%)	4.3	13.2	7.8	0.52
<30 m of stream channel				
Area (km^2)	0.2	0.02	0.08	0.01
Forest (%)	0	99	53	6.3
Cropland/pasture (%)	100	1	46	7.2
Slope (%)	4.0	10.8	7.1	0.38
Base flow				
DRP ($mg\,l^{-1}$)	0.016	0.073	0.032	0.003
PP ($mg\,l^{-1}$)	0.039	0.230	0.098	0.012
TP ($mg\,l^{-1}$)	0.084	0.276	0.146	0.013
SS ($g\,l^{-1}$)	0.074	0.351	0.163	0.014
Storm flow				
DRP ($mg\,l^{-1}$)	0.053	0.430	0.161	0.024
PP ($mg\,l^{-1}$)	0.212	1.845	0.769	0.084
TP ($mg\,l^{-1}$)	0.384	1.971	0.968	0.084
SS ($g\,l^{-1}$)	0.200	2.072	0.727	0.095

[a] One standard error of the mean.
[b] The WE-38 catchment is in 10% pasture, 25% corn, 15% soybean, 13% wheat, oats, and barley, and 7% alfalfa.

1088 km^2 in southwest Finland, Ekholm et al. (2000) found that the quantity of total P and suspended sediment was a function of fields in agriculture (largely cropped).

Within WE-38 sub-catchments, the proportion of land in cropland varied from 5 to 96% of total area, whereas forest varied from 4 to 95% of total area (Table 3). Following a correlation analysis, significant coefficients were found between the total land area in cropland and mean TP concentration in storm flow ($r = 0.58^{*}$). Interestingly, the correlation between mean PP concentration and land in cropland was stronger ($r = 0.67^{**}$), indicating the significance of mean suspended sediment concentration in P transport during storm flow. Indeed mean suspended sediment concentration was also correlated to land area in cropland ($r = 0.78^{***}$). To a lesser degree of significance, mean PP and SS concentrations were also correlated to land in forest ($r = 0.46^{*}$ and $r = 0.56^{**}$, respectively). However, of more interest was the absence of any relationship between slope within WE-38 sub-catchments and mean P or suspended sediment concentrations in storm flow.

The accepted logic is that the loss of P and sediment from fields is much greater in areas of greater slope (e.g. Ekholm et al., 2000; Sliva and Williams, 2001). However, this phenomenon is not expressed in the WE-38 catchment, as most steep land within the sub-catchments is in forest, which tends to lose much less P than cropland (Fig. 3; Peterjohn and Correll, 1984; Sliva and Williams, 2001). Clearly, land use in WE-38 is more dominant than slope in influencing P loss in stream flow. As such, mitigation strategies like conservation tillage or manure management should prove effective in minimizing P loss in the studied sub-catchments.

Other mitigation strategies, such as riparian or stream buffers, function on the premise that areas immediately adjacent to the stream are most active in controlling P losses. Indeed there is much evidence to support this by decreasing the load of P transport by such mechanisms as saturation-excess overland flow (e.g. Gburek and Sharpley, 1998; McDowell et al., 2001), or subsurface flow (e.g. McDowell and Sharpley, 2001b). However, contrary to other studies (e.g. Sliva and Williams, 2001), when land use and

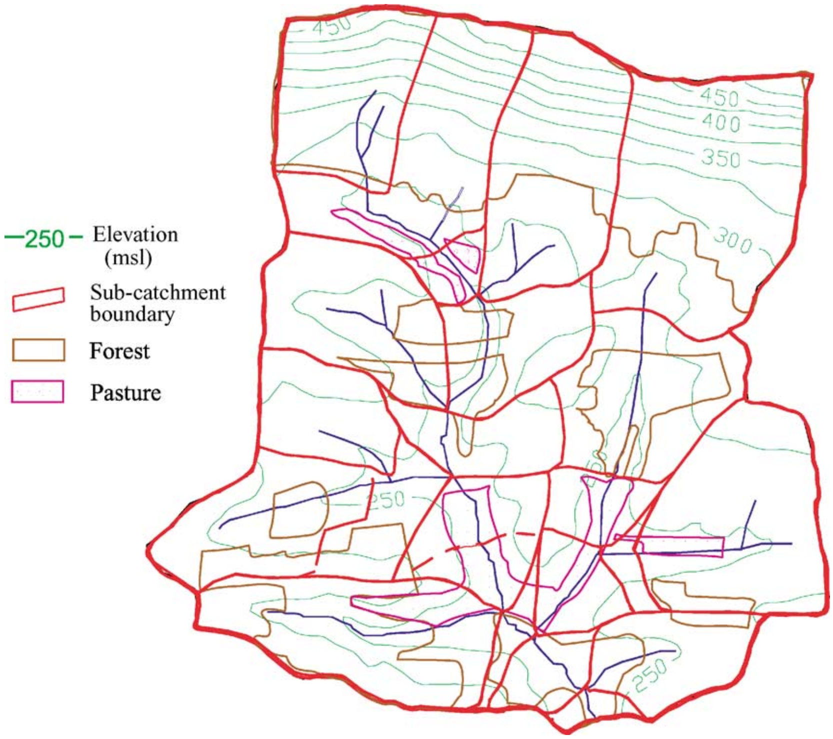

Fig. 3. Land use and slope within each sub-catchment showing the dominance of forested land in areas with close contour lines (i.e. steep). Areas in white are cropland.

slope within 30 m of the stream channel were examined relative to P fractions in storm flow, no relationships were found. The exact reason for this is unclear. However, a large number of possibilities could explain the phenomenon such as:

- The resuspension of stream-bed sediment into the flowing water column.
- Influence of other management factors such as manure applications. Recent evidence has suggested that this can be a dominant factor in P loss in overland flow even from areas in excess of 100 m away from the stream channel (McDowell and Sharpley, 2002a).
- Variable P losses in subsurface flow that are less affected by the near stream channel land use. For example, the loss of P in tile-drains and their direct connectivity to streams is known to be a significant source of P loss (Sims et al., 1998). Such drains are known to occur at various locations within the catchment.
- Mean base flow for all P fractions was unrelated to either land use or slope. Consideration of only areas within 30 m of the stream channel did not change this. This lends further support of the control of P during base flow by fluvial sediments as per Fig. 2. In another paper, McDowell et al. (2001) studied in more depth the processes occurring during base and storm flow in a sub-catchment (39.5 ha) of WE-38. The findings were that during storm flow, areas of P loss were defined by a combination of erodibility and landscape soil P concentration. In addition, the movement of soil from the landscape into the stream then helped define the EPC_0 of the fluvial sediment and the P concentration in base flow.

3.4. Perspectives

The approach used here looked at two of the major factors important in defining P loss, namely land use and slope (e.g. Ekholm et al., 2000). These were deemed to be parameters that would require a minimum of groundwork to generate a plausible answer. Digital elevation models (DEM), used to generate slope data within a geographical information system are widely available, as are aerial photographs, which help define broad land use categories. However, it is clear that other factors are more dominant, especially for determining base flow concentrations. These could include a combination of:

- The dominance of management factors (e.g. manure spreading) in determining the potential for seasonal and sudden (incidental) P loss patterns and their buffering by fluvial sediments (Preedy et al., 2001; Owens and Walling, 2002; McDowell et al., 2002).
- The distribution of P within the landscape.
- Limited data set (e.g. the scale of the DEM or P loss data).

This study indicates that a blanket approach to predict base flow P loss per se on a whole catchment or near stream area basis cannot be recommended. However, there is potential for such an approach to predict the potential for storm flow losses. Such information is valuable when considering the redistribution of P rich sediment from one area where it may not be a problem to another area where it may be, such as an anaerobic stratum within a reservoir. In contrast, freshwater systems buffer themselves to sudden inputs of P to such a degree that a gradual buildup of P within the system is the defining criterion for potential eutrophication and water quality problems (Correll, 1998). Furthermore, it is clearly evident that for the determination of long-term buffering potential of P inputs by a freshwater system, the distribution and P enrichment of fluvial sediments must also be considered. Only then can a successful assessment be made of the potential for P losses to actually cause eutrophication problems in a water body.

In terms of environmental management of P to minimize accelerated eutrophication within the catchment, mean TP concentrations in both base ($0.146\,\mathrm{mg\,l^{-1}}$) and storm flow ($0.968\,\mathrm{mg\,l^{-1}}$) (Table 3), exceed eutrophic criteria ($0.146\,\mathrm{mg\,l^{-1}}$ as total P) established for stream or other flowing waters not discharging directly into lakes or impoundments (Dodds et al., 1998; USEPA, 1994). Clearly, some of the remedial strategies outlined earlier, which include conservation tillage, buffers, and manure management, need to be implemented within the catchment to minimize P export, especially as much TP was as PP; approximately 67% in base flow and 79% in storm flow (Table 3).

4. Conclusions

Concentrations of P and other parameters, such as organic matter and Al and Fe, influencing P uptake and release to stream flow were found to vary greatly not only within a single stream reach, but also within flow regimes. Total P of tributaries was greater than below confluences, whereas the opposite was true of P release rate, presumably due to physical disturbance and the presence of more sand-sized particles with lesser P affinity than fine-sized particles. In addition to flow regimes, the proportions of forest or cropland and pasture within each of the sub-catchments was related to the concentration of plant available P (Mehlich-3 extractable P) in sediments. Slopes within the sub-catchments were not related to Mehlich-3 sediment P.

During base flow, sufficient time was available for the sediments to establish quasi-equilibrium with flowing water. However, during storm flow, P concentrations were unrelated to any parameters controlling P release from the sediments. Moreover, storm flow P concentrations were correlated to the different proportions of cropland and forest or pasture, suggesting the transport of P from the landscape was an influence. When data for land use and slope for near stream areas (thought to be very active in controlling P loss) were considered relative to P in stream flow, no relationship could be derived. This indicated that management and the distribution of P from outside this area was clearly a factor. Thus, consideration of landscape variables, such as land use and slope alone, was insufficient to gain an accurate picture of P loss and the potential for water quality impairment. Furthermore, for this to be successful, future assessment must take into account the role and distribution of fluvial sediments as a source of sustained P release and thus, their likely influence on downstream water quality.

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